EXPRESS MAIL LABEL NUMBER EL822429368US

Form PTO-1390 REV.10-94) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEYS DOCKET NUMBER **RN99013**
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.5) NOT APPLICABLE 09/890944
INTERNATIONAL APPLICATION NO. **PCT/FR00/00371**	INTERNATIONAL FILING DATE **February 15, 2000**	PRIORITY DATE CLAIMED **February 17, 1999**

TITLE OF INVENTION
USE OF FILM-FORMING TITANIUM DIOXIDE DISPERSIONS FOR CLEANING AND DISINFECTING SURFACES, FILM-FORMING TITANIUM DIOXIDE DISPERSIONS

APPLICANT (S) FOR DO/EO/US:
Eric AUBAY , Thierry CHOPIN , Cédric GEFFROY, Veronique GUILLOU, and CORINNE LEHAUT

Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1 ☒ This is a **FIRST** submission of items concerning a filing under 35 U S C 371
2 ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U S C 371
3 ☒ This express request to begin national examination procedures (35 U S C 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371 (b) and PCT Articles 22 and 39(1)
4 ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date

5 ☒ A copy of the International Application as filed (35 U S C 371(c)(2))
  a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
  b. ☒ has been transmitted by the International Bureau.
  c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6 ☒ A translation of the International Application into English (35 U S C 371(c)(2)).

7 ☒ A copy of the International Search Report (PCT/ISA/210)

8 ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(2)).
  a. ☐ are transmitted herewith (required only if not transmitted by the International
  b. ☐ have been transmitted by the International Bureau
  c. ☐ have not been made, however the time limit for making such amendments has NOT expired.
  d. ☒ have not been made and will not be made.

9 ☐ A translation of the amendments to the claims under PCT Article 19 (35 U S C 371(c)(3)).

10 ☒ A oath or declaration of the inventor(s) (35 U S C 371(c)(4)). **(unsigned)**

11 ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).

12 ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)).

Items 13 to 18 below concern document(s) or information included:

13 ☒ An information Disclosure Statement under 37 CFR 1 97 and 1 98

14 ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3 28 and 3 31 is included

15 ☒ A FIRST preliminary amendment

16 ☐ A SECOND or SUBSEQUENT prelimina amendment

17 ☐ A substitute specification.

18 ☐ A change of power of attorney and/or address letter

19 ☒ Certificate of Mailing by Express Mail

20 ☒ Other items or information

Forms PCT/IB/308 and 332, PCT/ISA/ 210 (English & French Version), PCT/IPEA/ 409, PCT/FR00/00371 as published

JC05 Rec'd PCT/PTO 0 7 AUG 2001

US APPLICATION NO (IF KNOWN, SEE 37 CFR 1.5) 09/890944	International Application No. PCT/FR00/00371	ATTORNEY DOCKET NUMBER RN99013

CALCULATIONS PTO ONLY

21 The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):

☐ Neither international preliminary examination fee (37 CFR 1,482) nor International search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO..... **$1,000.00**

☒ International preliminary examination fee not paid to USPTO but International Search Report prepared by the EPO or JPO..... **$ 860.00**

☐ International preliminary examination fee (37 CFR 1,482) not paid to USPTO but international search (37 CFR 1,4445 (a)(2)) fee paid to USPTO..... **$ 710.00**

☐ International preliminary examination fee paid to USPTO (37 CFR 1,482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... **$ 690.00**

☐ International preliminary examination fee paid to USPTO (37 CFR 1,482) and all claims satisfied provisions of PCT Article 33(2)-(4) ..... **$ 100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT = **$ 860.00**

Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1,492(e)). **$ 0.00**

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total Claims	55-20=	35	X$18.00	$ 630.00
Independent Claims	2-3=	0	X$80.00	$ 0.00
MULTIPLE DEPENDENT CLAIMS(S) (if applicable) N/A			☐	$ 0.00
			TOTAL OF ABOVE CALCULATIONS =	$ 1,490.00
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) ☐				$ 0.00
			SUBTOTAL =	$ 1,490.00
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1,492 (f)).		+		$ 0.00
			TOTAL NATIONAL FEE =	$ 1,490.00
Fee for recording the enclosed assignment (37 CFR1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property + ☐				$ 0.00
			TOTAL FEES ENCLOSED =	$ 1,490.00
			Amount to be refunded	$
			charged	$

a ☐ A check in the amount of $_____ to cover the above fees is enclosed

b ☒ Please charge my Deposit Account No. **18-1171** in the amount of **$1,490.00** to cover the above fees.

c ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. **18-1171** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1,494 or 1,495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

John Daniel WOOD
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259 Prospect Plains Road
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SIGNATURE

John Daniel WOOD
NAME

31,146
REGISTRATION NUMBER

August 6 , 2001
DATE

Express Mail Label #: EL822429368US

Case **RN99013**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Eric AUBAY , Thierry CHOPIN , Cédric GEFFROY, Veronique GUILLOU, and **CORINNE LEHAUT**
National Phase of PCT/FR00/00371 **Examiner: To be assigned**
International Filing Date : February 15, 2000
Serial No: To be assigned **Art Unit: To be assigned**
Filing Date: To be assigned
For: USE OF FILM-FORMING TITANIUM DIOXIDE DISPERSIONS FOR CLEANING AND DISINFECTING SURFACES, FILM-FORMING TITANIUM DIOXIDE DISPERSIONS

Assistant Commissioner for Patents

Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the specification and claims:

In the specification:

Page 1, just after the title, please add the new following amendment:

This application is an application under 35 U.S.C. Section 371 of International Application Number PCT/FR00/00371 filed on February 15, 2000.

In the claims:

Please cancel claims 1 to 33 and replace them with the new following claims 34 to 88 :

34) (New) A process for cleaning or disinfecting surfaces exposed to light, comprising the step of depositing a film of titanium dioxide on said surfaces with a film-forming dispersion comprising a continuous phase, said titanium dioxide

being in the form of elementary particles whose size is less than 100 nm, and whose specific surface area is greater than 150 m^2/g, the continuous phase of said dispersion comprising water or at least one alcohol whose boiling point is less than 120°C, and said dispersion having, when it comprises water, a pH different by at least 1 unit, from the value of the isoelectric point of titanium dioxide in said dispersion.

35) (New) A process according to claim 34), wherein the size of the particles is less than 70 nm, the specific surface area of the particles is greater than 200 m^2/g, the boiling point of the alcohol is less than or equal to 100°C, and the pH is different by at least 2 units, from the value of the isoelectric point of titanium dioxide in the dispersion.

36) (New) A process according to claim 34), wherein the size of the particles is from 20 to 60 nm, and the specific surface area is from from 200 to 300 m^2/g.

37) (New) A process according to claim 34) wherein the particles of titanium dioxide are anatase.

38) (New) A process according to claim 34) wherein the dispersion comprises from 0.01 to 15% of its weight of titanium dioxide.

39) (New) A process according to claim 34) wherein the dispersion comprises from 0.1 to 10% of its weight of titanium dioxide.

40) (New) A process according to claim 34) wherein the continuous phase comprises an aliphatic monoalcohol whose boiling point is less than 100°C.

41) (New) A process according to claim 34) wherein the continuous phase comprises water.

42) (New) A process according to claim 41) wherein the continuous phase comprises from 50 to 100% water.

43) (New) A process according to claim 42) wherein the continuous phase comprises from 70 to 99.9% water.

44) (New) A process according to claim 41) wherein the dispersion has a pH of from 0 to 14.

45) (New) A process according to claim 42) wherein the dispersion has a pH of from 2 to 14.

46) (New) A process according to claim 44), wherein the pH of the dispersion is less than 4 or more than 8, when the dispersion does not comprise an additive modifying the isoelectric point of titanium dioxide.

47) (New) A process according to claim 46), wherein the pH of the dispersion is from 0 to 3, or from 9 to 14, when the dispersion does not comprise an additive modifying the isoelectric point of titanium dioxide.

48) (New) A process according to claim 34) wherein the dispersion further comprises at least one film-forming organic or organosiloxane polymer.

49) (New) A process according to claim 48) wherein the dispersion comprises from 0.005 to 15% of the film-forming polymer.

50) (New) A process according to claim 49) wherein the dispersion comprises from 0.01 to 10% of the film-forming polymer.

51) (New) A process according to claim 48) wherein the film-forming polymer is selected from the group consisting of:

- terephthalic oligoesters or copolyesters, optionally sulfonated,
- polyoxyalkylenated polymers which carry anionic functions,
- cationic polymers,
- amphoteric polymers,
- polyalkoxylated polydimethylsiloxanes, and
- film-forming polymers derived from ethylenically unsaturated monomers polymerizable by radical means.

52) (New) A process according to claim 51), wherein the film-forming polymer interacts with the surface of the titanium dioxide particles by electrostatic bonding.

53) (New) A process according to claim 52) wherein the polymer is selected from the group consisting of:

- a sulfonated terephthalic oligoester or copolyester,
- a polyoxyalkylenated polymer which carries anionic functions,
- a cationic polymer additionally exhibiting bacteriostatic properties,
- a cationic homopolymer or copolymer derived from at least one cationic monomer comprising an ethylenic unsaturation, optionally in a mixture with at least one nonionic monomer, and

- an amphoteric copolymer derived from at least one cationic monomer comprising an ethylenic unsaturation, and at least one anionic monomer comprising an ethylenic unsaturation, optionally in a mixture with at least one nonionic monomer.

54) (New) A process according to claim 52) wherein the film-forming polymer is selected from the group consisting of:

- copolymers of acrylic acid or methacrylic acid and polyethylene glycol acrylate or methacrylate having a polyoxyethylene mass of from 500 to 10 000,
- quaternary ammonium ionenes,
- cationic polymers derived from epichlorohydrin and dimethylamine, and
- cationic polymers derived from epichlorohydrin and imidazole

55) (New) A process according to claim 53) wherein the cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- aminoacryloyl or -acryloyloxy monomers,
- N,N-dialkyldiallylamine monomers
- polyquaternary monomers.

56) (New) A process according to claim 55) wherein the cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

trimethylaminopropyl methacrylate chloride, trimethylaminoethylacrylamide or trimethylaminomethacrylamide chloride or bromide, trimethylaminobutylacrylamide or trimethylaminobutylmethacrylamide methyl sulfate, trimethylaminopropyl-

methacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl trimethylammonium chloride or methyl sulfate, acryloyloxyethyltrimethylammonium chloride, 1-ethyl-2-vinylpyridinium bromide, 1-ethyl-2-vinylpyridinium chloride, 1-ethyl-2-vinylpyridinium bromide methyl sulfate, N,N-dimethyldiallylammonium chloride (DADMAC), dimethylaminopropylmethacrylamide chloride, and N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT)

57) (New) A process according to claim 53) wherein the anionic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- acrylic, methacrylic, fumaric, maleic, itaconic, N-methacroylalanine, or N-acryloylhydroxyglycine acids or anhydrides, or their water-soluble salts, and
- water-soluble sulfonated or phosphonated ethylenically unsaturated monomers.

58) (New) A process according to claim 57) wherein the anionic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

sulfopropyl acrylate, its water-soluble salts, water-soluble styrenesulfonates, vinylsulfonic acid, its water-soluble salts, vinylphosphonic acid, and its water-soluble salts.

59) (New) A process according to claim 53) wherein the nonionic monomer is selected from the group consisting of acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohols, alkyl acrylates or methacrylates, hydroxyalkyl acrylates or methacrylates, and polyoxyalkylene glycol acrylates or methacrylates.

60) (New) The use as claimed in claim 53) wherein the cationic or amphoteric polymer derived from at least one cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- a DIQUAT homopolymer;
- a DADMAC homopolymer;
- a MAPTAC/acrylic or methacrylic acid; a DIQUAT/acrylic or methacrylic acid; a DADMAC/acrylic or methacrylic acid copolymer;
- a MES/acrylic or methacrylic acid/DMAEMA copolymer;
- a MAPTAC/acrylic acid/acrylamide; a MAPTAC/maleic anhydride/acrylamide; a MAPTAC/vinylsulfonic acid/acrylamide copolymer;
- a DADMAC/acrylic acid/acrylamide; a DADMAC/maleic anhydride/acrylamide; a DADMAC/vinylsulfonic acid/acrylamide copolymer;
- a DIQUAT/acrylic acid/acrylamide; a DIQUAT/maleic anhydride/acrylamide; and a DIQUAT/vinylsulfonic acid/acrylamide copolymer;

copolymers having a ratio of the total number of anionic charges to the total number of cationic charges of from 95/5 to 5/95,

61) (New) A process according to claim 60) wherein the ratio is from 90/10 to 10/90.

62) (New) A process according to claim 53) wherein the dispersion comprises from 0.01 to 2% by weight of the film-forming polymer interacting with the surface of the titanium dioxide particles by electrostatic bonding.

63) (New) A process according to claim 52), wherein the dispersion comprises water and has a pH of from 4 to 9.

64) (New) A process according to claim 34) wherein the amount of titanium dioxide deposited on the surfaces is from 0.01 to 10 g of titanium dioxide per m^2 of the surface to be treated.

65) (New) A process according to claim 64) wherein the amount of titanium dioxide deposited on the surfaces is from 0.05 to 5 g of titanium dioxide per m^2 of the surface to be treated.

66) (New) A film-forming dispersion comprising:

- from 0.01 to 15% of its weight of titanium dioxide in the form of elementary particles whose size is less than 100 nm, and whose specific surface area is greater than 150 m^2/g,
- from 0.005 to 15% of its weight of at least one film-forming polyalkoxylated organosiloxane or organic polymer, and
- a continuous phase of said dispersion comprising water or at least one alcohol whose boiling point is less than 120°C, and having, when it comprises water, a pH different

by at least 1 unit, from the value of the isoelectric point of titanium dioxide in said dispersion.

67) (New) A film-forming dispersion according to claim 64, wherein the size of the particles is less than 70 nm, the specific surface area of the particles is greater than 200 m^2/g, the boiling point of the alcohol is less than or equal to 100°C, and the pH is different by at least 2 unit, from the value of the isoelectric point of titanium dioxide in the dispersion.

68) (New) A film-forming dispersion according to claim 66), characterized in that the titanium dioxide is in the form of elementary particles whose size is of the order of from 20 to 60 nm and whose specific surface area is of the order of from 200 to 300 m^2/g.

69) (New) A film-forming dispersion according to claim 66), wherein the particles of titanium dioxide are anatase.

70) (New) A film-forming dispersion according to claim 66), wherein the continuous phase comprises an aliphatic monoalcohol whose boiling point is less than 100°C.

71) (New) A film-forming dispersion according to claim 66), wherein the continuous phase comprises water.

72) (New) A film-forming dispersion according to claim 71) wherein the continuous phase comprises from 50 to 100% water.

73) (New) A film-forming dispersion according to claim 72) wherein the continuous phase comprises from 70 to 99.9% water.

74) (New) A film-forming dispersion according to claim 71) wherein the dispersion has a pH of from 0 to 14.

75) (New) A film-forming dispersion according to claim 74) wherein the dispersion has a pH of from 2 to 14.

76) (New) A film-forming dispersion according to claim 66), wherein the film-forming polymer is selected from the group consisting of:

- terephthalic oligoesters or copolyesters, optionally sulfonated,
- polyoxyalkylenated polymers which carry anionic functions,
- cationic polymers,
- amphoteric polymers,
- polyalkoxylated polydimethylsiloxanes, and
- film-forming polymers derived from ethylenically unsaturated monomers polymerizable by radical means.

77) (New) A film-forming dispersion according to claim 76) wherein the film-forming polymer interacts with the surface of the titanium dioxide particles by electrostatic bonding.

78) (New) A film-forming dispersion according to claim 77) wherein the polymer is selected from the group consisting of:

- a sulfonated terephthalic oligoester or copolyester,
- a polyoxyalkylenated polymer which carries anionic functions,
- a cationic polymer additionally exhibiting bacteriostatic properties,

- a cationic homopolymer or copolymer derived from at least one cationic monomer comprising an ethylenic unsaturation, optionally in a mixture with at least one nonionic monomer, and

- an amphoteric copolymer derived from at least one cationic monomer comprising an ethylenic unsaturation, and at least one anionic monomer comprising an ethylenic unsaturation, optionally in a mixture with at least one nonionic monomer.

79) (New) A film-forming dispersion according to claim 77) wherein the film-forming polymer is selected from the group consisting of:

- copolymers of acrylic acid or methacrylic acid and polyethylene glycol acrylate or methacrylate having a polyoxyethylene mass of from 500 to 10 000,
- quaternary ammonium ionenes,
- cationic polymers derived from epichlorohydrin and dimethylamine, and
- cationic polymers derived from epichlorohydrin and imidazole

80) (New) A film-forming dispersion according to claim 78) wherein the cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- aminoacryloyl or -acryloyloxy monomers,
- N,N-dialkyldiallylamine monomers
- polyquaternary monomers.

81) (New) A film-forming dispersion according to claim 80) wherein the cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

trimethylaminopropyl methacrylate chloride, trimethylaminoethylacrylamide or trimethylaminomethacrylamide chloride or bromide, trimethylaminobutylacrylamide or trimethylaminobutylmethacrylamide methyl sulfate, trimethylaminopropyl-methacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl trimethylammonium chloride or methyl sulfate, acryloyloxyethyltrimethylammonium chloride,
1-ethyl-2-vinylpyridinium bromide, 1-ethyl-2-vinylpyridinium chloride, 1-ethyl-2-vinylpyridinium bromide methyl sulfate,
N,N-dimethyldiallylammonium chloride (DADMAC),
dimethylaminopropylmethacrylamide chloride, and
N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT)

82) (New) A film-forming dispersion according to claim 78) wherein the anionic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- acrylic, methacrylic, fumaric, maleic, itaconic, N-methacroylalanine, or N-acryloylhydroxyglycine acids or anhydrides, or their water-soluble salts, and
- water-soluble sulfonated or phosphonated ethylenically unsaturated monomers.

83) (New) A film-forming dispersion according to claim 82) wherein the anionic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

sulfopropyl acrylate, its water-soluble salts, water-soluble styrenesulfonates, vinylsulfonic acid, its water-soluble salts, vinylphosphonic acid, and its water-soluble salts.

84) (New) A film-forming dispersion according to claim 78) wherein the nonionic monomer is selected from the group consisting of acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohols, alkyl acrylates or methacrylates, hydroxyalkyl acrylates or methacrylates, and polyoxyalkylene glycol acrylates or methacrylates.

85) (New) A film-forming dispersion according to claim 78) wherein the cationic or amphoteric polymer derived from at least one cationic monomer comprising an ethylenic unsaturation is selected from the group consisting of:

- a DIQUAT homopolymer;
- a DADMAC homopolymer;
- a MAPTAC/acrylic or methacrylic acid; a DIQUAT/acrylic or methacrylic acid; a DADMAC/acrylic or methacrylic acid copolymer;
- a MES/acrylic or methacrylic acid/DMAEMA copolymer;
- a MAPTAC/acrylic acid/acrylamide; a MAPTAC/maleic anhydride/acrylamide; a MAPTAC/vinylsulfonic acid/acrylamide copolymer;
- a DADMAC/acrylic acid/acrylamide; a DADMAC/maleic anhydride/acrylamide; a DADMAC/vinylsulfonic acid/acrylamide copolymer;

- a DIQUAT/acrylic acid/acrylamide; a DIQUAT/maleic anhydride/acrylamide; and a DIQUAT/vinylsulfonic acid/acrylamide copolymer;

copolymers having a ratio of the total number of anionic charges to the total number of cationic charges of from 95/5 to 5/95,

86) (New) A film-forming dispersion according to claim 85) wherein the ratio is from 90/10 to 10/90.

87) (New) A film-forming dispersion according to claim 78), wherein the dispersion comprises from 0.01 to 2% by weight of the film-forming polymer interacting with the surface of the titanium dioxide particles by electrostatic bonding.

88) (New) A film-forming dispersion according to claim 77), wherein the dispersion comprises water and has a pH of from 4 to 9.

REMARKS

The preliminary amendments are filed to comply with the claims structure and wording according to the United States Patent law. It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed.

New claims find basis as mentioned in the chart below:

New Claims	Basis	
	In the claims as filed	**In the specification**
34, 35	1	"film forming" on page 1, lines 19-20
36	2	
37	3	
38, 39	4	
40	5	
41	6	
42, 43	7	
44, 45	8	
46, 47	9	
48	10	
49, 50	11	
51	12	
52	13	
53-59	14	
60, 61	15	
62	16	
63	17	
64, 65	32	
66, 67	18	
68	19	
69	20	
70	21	
71	22	
72, 73	23	
74,75	24	
76	25	
77	26	
78-84	27	
85, 86	28	
87	29	
88	30	

Entry of the amendments is respectfully requested.

Respectfully submitted,

By: John Daniel Wood

August 6 , 2001

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F/Brevet/RN999013JDW.prelim

USE OF FILM-FORMING TITANIUM DIOXIDE DISPERSIONS FOR CLEANING AND DISINFECTING SURFACES, FILM-FORMING TITANIUM DIOXIDE DISPERSIONS

The present invention relates to the use of a film-forming dispersion of titanium dioxide nanoparticles for cleaning and/or disinfecting surfaces exposed to light. The invention also relates to a process for cleaning and/or disinfecting surfaces exposed to light by depositing on said surfaces a film of titanium dioxide nanoparticles, and to titanium dioxide nanoparticle dispersions whose film-forming properties are improved by the presence of a film-forming polymer.

The use of titanium dioxide nanoparticles as a bactericidal and photooxidizing agent in detergent compositions for the washing of laundry or of surfaces was described by the Applicant in its French patent application No. 95 00821 of January 25, 1996.

The Applicant has observed that titanium dioxide nanoparticle dispersions are film-forming.

The object of the present invention is to utilize the photooxidizing properties of titanium dioxide nanoparticles and their film-forming nature to clean and/or disinfect surfaces on said surfaces of an impermanent film of titanium dioxide capable under light of generating free radicals which disinfect the surfaces and oxidize the soiling.

The creation of this film makes it possible

- to clean (remove soiling)
- to control or even suppress bacterial proliferation between two operations of disinfecting by conventional means;
- to reduce the frequency of cleaning or disinfection and/or the quantity of cleaning or disinfecting products presently used.

The film formed is then progressively removed by the subsequent cleaning steps. The target fields of application may be very varied, such as the cleaning or disinfecting of hard surfaces encountered in the food industry, kitchens, bathrooms, washrooms, hospitals, glazing, facades, etc, and also the breakdown and/or removal of heavy hydrocarbons deposited on surfaces, particularly following accidental pollution (for example beaches, rocks, equipment, plants, etc).

The invention first provides for the use of a titanium dioxide dispersion for cleaning and/or disinfecting surfaces exposed to light by deposition of a film of titanium dioxide on said surfaces, said titanium dioxide being in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g, the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is less than 120°C, preferably less than or equal to 100°C, said dispersion having, when it comprises water,

a pH different by at least 1 unit, preferably by at least 2 units, from the value of the isoelectric point of titanium dioxide in said dispersion.

The pH of the dispersion comprising water is of course the pH of the continuous phase.

The titanium dioxide employed is very particularly in the form of elementary particles whose size is of the order of from 20 to 60 nm and whose specific surface area is of the order of from 200 to 300 m^2/g.

The specific surface area given is a BET surface. By BET surface is meant the specific surface area determined by nitrogen adsorption in accordance with the standard ASTM D 3663-78, based on the Brunauer - Emmett - Teller method described in the journal "The Journal of the american Society",60, 309 (1938).
The size of the elementary particles of titanium dioxide according to the invention is measured by transmission electron microscopy (TEM).

The nature of the elementary particles of titanium dioxide is preferably anatase (isoelectric point between 5.5 and 6 for pure anatase).
Within said dispersion, said elementary particles may be present in the form of both aggregates and elementary particles.

For effective implementation of the invention, said dispersion may comprise in the order of from 0.01 to 15% of its weight, preferably in the order

of from 0.1 to 10% of its weight, of titanium dioxide.

Among the alcohols which may constitute or be present in the continuous phase, mention may be made in particular of aliphatic monoalcohols whose boiling point is less than 100°C such as ethanol, isopropanol, etc.

When the continuous phase consists of a water/alcohol(s) mixture whose boiling point is less than 120°C, the ratio between the water and the alcohol or alcohols is arbitrary.

A high boiling point alcohol (in particular a diol such as ethylene glycol) may, however, be present in the continuous phase, but may not represent more than 10% of the weight of said phase.

Preferentially, the continuous phase comprises water, preferably from 50 to 100%, preferably from 70 to 99.9% of its weight of water.

When the continuous phase comprises water, the pH values favorable to effective implementation of the invention may range from 0 to 14, preferably from 2 to 14, and are a function of other additives which may be present in the dispersion and capable of modifying the isoelectric point of the titanium dioxide.

When no additive capable of modifying the isoelectric point of titanium dioxide is present, the pH values favorable to effective implementation of the invention are situated below 4 or above 8; preferentially, the pH of the dispersion may range from 0 to 3 approximately

or from 9 to 14 approximately.

If necessary, pH regulators may be present; mention may be made of mineral acids or organic acids such as hydrochloric, nitric, sulfuric, phosphoric, citric, glutaric, adipic and succinic acids, etc., and bases such as aqueous ammonia, alkali metal hydroxides, sodium carbonate, and triethanolamine, etc.

Said dispersion may further comprise other additives which are soluble or dispersible in the continuous phase, said additives possibly promoting its stability, wettability, augmenting its film-forming nature, its biocidal nature, or providing other supplementary properties.

Examples of additives which may be mentioned include:

- nonionic surfactants promoting wettability, of the polyoxyethylenated C_6-C_{12} alkylphenol type, polyoxypropylenated and/or polyoxyethylenated C_8-C_{22} aliphatic alcohol type, ethylene oxide-propylene oxide block copolymers, optionally polyoxyethylenated carboxylic amides, etc,
- anionic or amphoteric surfactants as dispersants, of the alkali metal soap type (alkali metal salts of C_8-C_{24} fatty acids), alkali metal sulfonates (C_8-C_{13} alkylbenzene sulfonates, C_{12}-C_{16} alkylsulfonates), sulfated and oxyethylenated C_6-C_{16} fatty alcohols, sulfated and oxyethylenated C_8-C_{13} alkylphenols type, alkali metal sulfosuccinates (C_{12}-C_{16} alkylsulfo-

succinates) etc, betaines, etc

- biocides or bacteriostatics capable of improving the biocidal nature of the dispersions, especially in the case of inadequate lighting, such as cationic surfactants (alkyldimethylammonium halides, etc), quaternary ammonium or phosphonium halide biocides, glycine-derivative amphoteric biocides, phenolic biocides, chlorhexidine-derivative biocides, hypochlorites, quaternary polyammonium film-forming polymers or biocides, etc

- film-forming antisoiling agents such as optionally sulfonated terephthalic polyesters, etc

- other film-forming homopolymers or copolymers such as those derived from monomers containing ethylenic unsaturation, especially cationic or amphoteric homopolymers or copolymers derived from cationic monomers containing ethylenic unsaturation

- film-forming polyoxyalkylene polymers which carry anionic functions

- film-forming polymers which impart brightness and oleophobicity, such as polyalkoxylated organopolysiloxanes, etc.

- fragrances

- dyes, etc.

These various additives may be present in a proportion of from 0 to 15% by weight of said dispersion.

One particular embodiment of the invention consists in improving the film-forming nature of the

titanium dioxide nanoparticles by the presence within the dispersion of at least one organic or organosiloxane polymer of film-forming nature which may further impart one or more supplementary properties to said dispersion.

The amount of polymer that may be present may represent in the order of from 0.005 to 15%, preferably in the order of from 0.01 to 10% of the weight of said dispersion.

Among the film-forming organic or organosiloxane polymers that may be employed, very particular mention may be made of:

- terephthalic polyesters additionally exhibiting antisoiling properties, such as

• polyester copolymers based on ethylene terephthalate and/or propylene terephthalate and polyoxyethylene terephthalate units (US-A-3 959 230, US-A-3 893 929, US-A-4 116 896, US-A-4 702 857, US-A-4 770 666);

• sulfonated polyester oligomers obtained by sulfonating an ethoxylated allyl alcohol-derived oligomer, dimethyl terephthalate and 1,2-propylenediol (US-A-4 968 451)

• polyester copolymers based on propylene terephthalate and polyoxyethylene terephthalate units and terminated with ethyl or methyl units (US-A-4 711 730) or polyester oligomers terminated with alkylpolyethoxy groups (US-A-4 702 857) or anionic sulfopolyethoxy (US-A-4 721 580) or sulfoaroyl groups (US-A-4 877 896)

• polyester-polyurethanes obtained by reacting a polyester obtained from adipic acid and/or terephthalic acid and/or sulfoisophthalic acid and a diol with a prepolymer containing terminal isocyanate groups obtained from a polyoxyethylene glycol and a diisocyanate (FR-A-2 334 698)

• sulfonated polyester oligomers obtained by condensing isophthalic acid, dimethyl sulfosuccinate and diethylene glycol (FR-A-2 236 926)

• polyester copolymers derived from dimethyl terephthalate, isophthalic acid, dimethyl sulfoisophthalate and ethylene glycol (EP-A-540374)

- cationic polymers further exhibiting bacteriostatic properties, such as

• the quaternary ammonium ionenes described in US-A-4,157,388 (MIRAPOL A-15 or POLYQUATERNIUM-2 from Rhodia)

• cationic polymers derived from epichlorohydrin and dimethylamine and those derived from epichlorohydrin and imidazole, such as GLOKILL PQ and ELC from Rhodia

- film-forming cationic or amphoteric homopolymers or copolymers derived from cationic monomers containing ethylenic unsaturation (described in more detail below)

- film-forming polyoxyalkylene polymers which carry anionic functions, such as copolymers of acrylic acid and/or methacrylic acid and polyethylene glycol acrylate and/or methacrylate whose polyoxyethylene unit has a mass of the order of from 500 to 10 000

- polyalkoxylated polydimethylsiloxanes which impart brightness and oleophobicity, such as SILICONE COPOLYOL 10646 from Rhodia

- other film-forming polymers derived from ethylenically unsaturated monomers polymerizable by radical means, such as (meth)acrylic acid, C1-C4 alkyl (meth)acrylates, styrene, butadiene, etc.

One very particularly advantageous embodiment of the invention consists in the use of titanium dioxide dispersions further comprising a film-forming organic polymer which is preferably hydrophilic and is capable of interacting with the surface of the titanium dioxide particles, preferably by electrostatic bonding.

Said dispersions are preferably aqueous and have a pH of the order of from 4 to 9.

They may comprise in the order of from 0.005 to 10%, preferably from 0.01 to 5%, very particularly from 0.01 to 2% by weight of film-forming organic polymer.

Among the film-forming polymers which may be present, mention may be made of:

* the sulfonated terephthalic copolyesters or oligoesters already mentioned above

* film-forming polyoxyalkylene polymers which carry anionic functions, such as copolymers of acrylic acid and/or methacrylic acid and polyethylene glycol acrylate and/or methacrylate whose polyoxyethylene unit has a mass of the order of from 500 to 10 000

* film-forming cationic polymers additionally exhibiting bacteriostatic properties, such as

• the quaternary ammonium ionenes described in US-A-4,157,388 (MIRAPOL A-15 or POLYQUATERNIUM-2 from Rhodia)

• cationic polymers derived from epichlorohydrin and dimethylamine and those derived from epichlorohydrin and imidazole, such as GLOKILL PQ and ELC from Rhodia

* film-forming cationic or amphoteric homopolymers or copolymers derived from cationic monomers containing ethylenic unsaturation.

By way of example of cationic film-forming homopolymers or copolymers derived from cationic monomers containing ethylenic unsaturation, mention may be made from those derived from at least one of the following cationic monomers

* aminoacryloyl or -acryloyloxy monomers such as trimethylaminopropyl methacrylate chloride, trimethylaminoethylacrylamide or -methacrylamide chloride or bromide, trimethylaminobutylacrylamide or -methacrylamide methyl sulfate, trimethylaminopropyl-methacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl trimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride;

* 1-ethyl-2-vinylpyridinium bromide, chloride or methyl

sulfate;

* N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC);

* polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride, N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT), etc;

optionally in a mixture with at least one nonionic monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or methacrylates, polyoxyalkylene glycol acrylates or methacrylates, etc.

Very particular mention may be made of DIQUAT homopolymers, such as MIRAPOL CLASTA from Rhodia, and DADMAC homopolymers, such as MIRAPOL 100 from Rhodia.

By way of example of amphoteric film-forming copolymers derived from cationic monomers containing ethylenic unsaturation, mention may be made of those derived from at least one of the abovementioned cationic monomers and at least one anionic monomer such as

* acrylic, methacrylic, fumaric, maleic, itaconic, N-methacroylalanine, N-acryloylhydroxyglycine, etc, acids or anhydrides, or their water-soluble salts;

* water-soluble sulfonated or phosphonated ethylenically unsaturated monomers, such as sulfopropyl

acrylate or its water-soluble salts, water-soluble styrene sulfonates, vinylsulfonic acid and its water-soluble salts or vinylphosphonic acid and its water-soluble salts, etc;

optionally in a mixture of at least one nonionic monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or methacrylates, polyoxyalkylene glycol acrylates or methacrylates, etc.

Very particular mention may be made of the following copolymers or terpolymers:

* MAPTAC/acrylic or methacrylic acid; DIQUAT/acrylic or methacrylic acid; DADMAC/acrylic or methacrylic acid;
* MES/acrylic or methacrylic acid/DMAEMA;
* MAPTAC/acrylic acid/acrylamide; MAPTAC/maleic anhydride/acrylamide; MAPTAC/vinylsulfonic acid/acrylamide;
* DADMAC/acrylic acid/acrylamide; DADMAC/maleic anhydride/acrylamide; DADMAC/vinylsulfonic acid/acrylamide;
* DIQUAT/acrylic acid/acrylamide; DIQUAT/maleic anhydride/acrylamide; DIQUAT/vinylsulfonic acid/acrylamide;

with a ratio of the total number of anionic charges to the total number of cationic charges of from 95/5 to 5/95, very particularly from 90/10 to 10/90.

Said cationic or amphoteric film-forming homopolymers or copolymers derived from cationic monomers containing ethylenic unsaturation preferably have a molecular mass of less than 100 000 (molecular mass by weight, expressed in g/mol, determinable by aqueous gel permeation chromatography (GPC) or measurement of the viscosity in 1N $NaNO_3$ solution.

The invention secondly provides a film-forming dispersion comprising

- in the order of from 0.01 to 15% of its weight, preferably in the order of from 0.1 to 10% of its weight of titanium dioxide in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 mg^2/g,
- and in the order of from 0.005 to 15% of its weight, preferably in the order of from 0.01 to 10% of its weight, of at least one film-forming polyalkoxylated organosiloxane or organic polymer,

the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is less than 120°C, preferably less than or equal to 100°C, and having, when it comprises water, a pH different by at least 1 unit, preferably at least 2 units, from the value of the isoelectric point of titanium dioxide in said dispersion.

Preferential or more particular features

regarding the nature of the titanium dioxide, the continuous phase, pH regulators, other additives that may be present, and respective amounts of various components, have already been indicated above.

Examples of film-forming alkoxylated organosiloxane or organic polymers which may be employed to improve the film-forming nature of the titanium nanoparticles have already been mentioned above.

Said dispersion may be obtained by mixing its various components at ambient temperature.

An especially advantageous film-forming dispersion comprises

- in the order of from 0.01 to 15% of its weight, preferably in the order of from 0.1 to 10% of its weight of titanium dioxide in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g,
- and in the order of from 0.005 to 10% of its weight, preferably in the order of from 0.01 to 5%, more particularly from 0.01 to 2% of its weight, of at least one film-forming organic polymer which is preferably hydrophilic and is capable of interacting with the surface of the titanium dioxide particles, preferably by electrostatic bonding,

the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point

is less than 120°C, preferably less than or equal to 100°C, and having, when it comprises water, a pH different by at least 1 unit, preferably at least 2 units, from the value of the isoelectric point of titanium dioxide in said dispersion.

They are preferably aqueous and have a pH of the order of from 4 to 9.

Examples of film-forming organic polymers which may be employed for interacting with the surface of the titanium dioxide particles, preferably by electrostatic bonding, have already been stated above.

The invention lastly provides a process for cleaning and/or disinfecting surfaces exposed to light by depositing and then drying on said surfaces a film-forming titanium dioxide dispersion, said titanium dioxide being in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g, the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is lower than 120°C, preferably lower than or equal to 100°C, said dispersion having, when it comprises water, a pH different by at least 1 unit, preferably by at least 2 units, from the value of the isoelectric point of titanium dioxide in the dispersion.

Preferential or more particular features regarding the nature of the titanium dioxide, the

continuous phase, pH regulators, other additives that may be present, especially film-forming polymers, and respective amounts of various components, have already been mentioned above.

The titanium dioxide nanoparticle dispersion may be deposited on these surfaces by fine spraying onto the surface to be treated, by application with the aid of a sponge, a cloth or with the aid of a preimpregnated cellulosic material, or any other means, in such a way as to deposit in the order of from 0.01 to 10 g of titanium dioxide per m^2 of the surface to be treated, preferably in the order of from 0.05 to 5 g of titanium dioxide per m^2 of the surface to be treated.

The examples which follow are given by way of illustration.

Example 1

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

15% dispersion of titanium dioxide (anatase) in ethylene glycol	3%
REPEL O TEX QCJ (15% aqueous dispersion of film-forming antisoiling ethylene terephthalate/polyoxyethylene terephthalate copolymer)	13%
isopropanol	47.5%
deionized water	36.5%

by introducing the film-forming antisoiling copolymer into the dispersion of titanium dioxide in ethylene glycol, followed by addition of the water/isopropanol mixture and then adjustment of the pH to 2.5 using hydrochloric acid.

Example 2

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

15% colloidal aqueous dispersion of titanium dioxide (anatase)	3%
REPEL O TEX QCJ (15% aqueous dispersion of film-forming antisoiling ethylene terephthalate/polyoxyethylene terephthalate copolymer)	3%
isopropanol	47%
deionized water	47%

by introducing the film-forming antisoiling copolymer into the colloidal aqueous dispersion of titanium dioxide, followed by addition of the water/isopropanol mixture and then adjustment of the pH to 2.5.

Example 3

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

15% colloidal aqueous dispersion of titanium dioxide	25%
REPEL O TEX QCJ (15% aqueous dispersion of film-forming antisoiling ethylene terephthalate/polyoxyethylene terephthalate copolymer)	8.3%
Isopropanol	33.3%
Deionized water	33.4%

by introducing the film-forming antisoiling copolymer into the colloidal aqueous dispersion of titanium dioxide, followed by addition of the water/isopropanol mixture and then adjustment of the pH to 2.5.

Example 4

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

15% colloidal aqueous dispersion of titanium dioxide	3%
SILICONE COPOLYOL 10646 (film-forming polyalkoxylated polydimethylsiloxane)	0.5%
isopropanol	47%
deionized water	49.5%

by introducing the film-forming polymer (imparting brightness and oleophobicity) into the colloidal aqueous dispersion of titanium dioxide, followed by addition of the water/isopropanol mixture and then adjustment of the pH to 2.5.

Example 5

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

15% colloidal aqueous dispersion of titanium dioxide	25%
GLOKILL PQ (50% by weight aqueous solution of film-forming bacteriostatic cationic polymer diluted to 15%)	8.3%
isopropanol	33.3%
deionized water	33.4%

by introducing the bacteriostatic film-forming polymer into the colloidal aqueous dispersion of titanium dioxide, followed by addition of the water/isopropanol mixture and then adjustment of the pH to 2.5.

Example 6

A dispersion is prepared of titanium dioxide (anatase) in the form of elementary particles of 40 nm whose specific surface area is 250 m^2/g after drying at 200°C, in a water/alcohol mixture, whose composition is as follows:

Reference	A	B
15% colloidal aqueous dispersion of titanium dioxide	3%	3%
GLOKILL PQ (cationic polymer)	0.1%	0%
isopropanol	5%	5%
deionized water	91.9%	92%

The pH of the dispersion is subsequently adjusted by adding sodium hydroxide to pH = 6.5.
In the presence of cationic polymer (test A) the dispersion remains homogeneous and the particle size

measurement by laser scattering confirms the absence of aggregation of titanium dioxide (particle size: 40 nm). In the case of the solution without cationic polymer (test B) severe precipitation is observed when sodium hydroxide is added.

The two neutralized solutions A and B are deposited on a black ceramic tile with the aid of adsorbent paper. The amount deposited is of the order of 0.5 mg/cm^2.

After drying in the open air, the solution A gives a layer of titanium invisible to the eye. In contrast, solution B gives very distinct white marks. Observation by optical microscopy confirms that the polymer allows an effective state of dispersion to be obtained during drying.

A model soil, stearic acid, is subsequently deposited on each ceramic tile which had been treated before and with formulas A and B. The layer of stearic acid is of approximately 0.01 mg/m^2 and it is obtained by depositing a 1% solution in isopropanol After drying, the tiles are exposed to visible light for 48 hours.

Following exposure, the ceramic tile treated with solution A has virtually no trace of stearic acid visible to the eye.

The tile treated with solution B exhibits visible traces of stearic acid.

Example 7

On a ceramic tile, a film corresponding to 3 or 6 g of titanium dioxide per m^2 of tile surface is formed by spreading the dispersion from example 2 over said tile using a film-drawing device.

The film is left to dry in ambient air overnight.

A suspension of bacteria (Pseudomonas Aeruginosa) is deposited over the entire surface of the tile.

The tile, covered with a UV-impervious cover (for the purpose of preventing excessive dehydration of the bacteria), is exposed to UV light (365 nm) for 6 hours.

The number of colonies is counted and compared with that obtained by depositing the same bacteria suspension on an untreated tile.

The results obtained are as follows:

Sample	**Titanium dioxide deposited (g/m^2)**	**Number of colonies (cfu/ml)**
Untreated tile	-	5×10^7
Treated tile	3	< 10
Treated tile	6	< 10

CLAIMS

1) The use of a titanium dioxide dispersion for cleaning and/or disinfecting surfaces exposed to light by deposition of a film of titanium dioxide on said surfaces, said titanium dioxide being in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g, the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is less than 120°C, preferably less than or equal to 100°C, said dispersion having, when it comprises water, a pH different by at least 1 unit, preferably by at least 2 units, from the value of the isoelectric point of titanium dioxide in said dispersion.

2) The use as claimed in claim 1), characterized in that the titanium dioxide is in the form of elementary particles whose size is of the order of from 20 to 60 nm and whose specific surface area is of the order of from 200 to 300 m^2/g.

3) The use as claimed in claim 1) or 2), characterized in that the elementary particles of titanium dioxide are anatase.

4) The use as claimed in any one of claims 1) to 3), characterized in that said dispersion comprises in the order of from 0.01 to 15% of its weight, preferably in the order of from 0.1 to 10% of

its weight, of titanium dioxide.

5) The use as claimed in any one of claims 1) to 4), characterized in that the alcohols which may constitute or be present in the continuous phase are aliphatic monoalcohols whose boiling point is less than 100°C.

6) The use as claimed in any one of claims 1) to 5), characterized in that the continuous phase comprises water.

7) The use as claimed in claim 6) characterized in that the continuous phase comprises from 50 to 100%, preferably from 70 to 99.9% of water.

8) The use as claimed in claim 6) or 7) characterized in that the dispersion has a pH of from 0 to 14, preferably from 2 to 14.

9) The use as claimed in claim 8), characterized in that the pH of the dispersion is situated at a value below 4 or above 8, preferably at a value of from 0 to 3 or from 9 to 14, when said dispersion is devoid of additive capable of modifying the isoelectric point of titanium dioxide.

10) The use as claimed in any one of claims 1) to 8), characterized in that said dispersion further comprises at least one film-forming organic or organosiloxane polymer.

11) The use as claimed in claim 10), characterized in that the amount of film-forming polymer represents in the order of from 0.005 to 15%,

preferably in the order of from 0.01 to 10% of said dispersion.

12) The use as claimed in claim 10) or 11), characterized in that said film-forming polymers are

- optionally sulfonated terephthalic oligoesters or copolyesters
- polyoxyalkylenated polymers which carry anionic functions
- cationic or amphoteric polymers
- polyalkoxylated polydimethylsiloxanes
- film-forming polymers derived from ethylenically unsaturated monomers polymerizable by radical means.

13) The use as claimed in claim 12) characterized in that said polymer is capable of interacting with the surface of the titanium dioxide particles by electrostatic bonding.

14) The use as claimed in claim 13) characterized in that said film-forming polymer is

- a sulfonated terephthalic oligoester or copolyester
- a polyoxyalkylenated polymer which carries anionic functions, such as copolymers of acrylic acid and/or methacrylic acid and polyethylene glycol acrylate and/or methacrylate whose polyoxyethylene unit has a mass of from 500 to 10 000
- a cationic polymer additionally exhibiting bacteriostatic properties, such as
  - quaternary ammonium ionenes
  - cationic polymers derived from epichlorohydrin and

dimethylamine and those derived from epichlorohydrin and imidazole

- a cationic homopolymer or copolymer derived from at least one cationic monomer containing ethylenic unsaturation: a monomer such as

* aminoacryloyl or -acryloyloxy monomers such as trimethylaminopropyl methacrylate chloride, trimethylaminoethylacrylamide or -methacrylamide chloride or bromide, trimethylaminobutylacrylamide or -methacrylamide methyl sulfate, trimethylaminopropyl-methacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl trimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride

* 1-ethyl-2-vinylpyridinium bromide, chloride or methyl sulfate

* N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC)

* polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride, N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT)

optionally in a mixture with at least one nonionic monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or

methacrylates, polyoxyalkylene glycol acrylates or methacrylates

- an amphoteric copolymer derived from at least one cationic monomer containing ethylenic unsaturation, a monomer like those mentioned above, and at least one anionic monomer containing ethylenic unsaturation, such as

* acrylic, methacrylic, fumaric, maleic, itaconic, N-methacroylalanine, N-acryloylhydroxyglycine acids or anhydrides or their water-soluble salts

* water-soluble sulfonated or phosphonated ethylenically unsaturated monomers, such as sulfopropyl acrylate or its water-soluble salts, water-soluble styrenesulfonates, vinylsulfonic acid and its water-soluble salts or vinylphosphonic acid and its water-soluble salts

optionally in a mixture with at least one nonionic monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or methacrylates, polyoxyalkylene glycol acrylates or methacrylates.

15) The use as claimed in claim 14) characterized in that said cationic or amphoteric polymer derived from at least one cationic monomer containing ethylenic unsaturation is

* a DIQUAT homopolymer

* a DADMAC homopolymer

* a MAPTAC/acrylic or methacrylic acid; DIQUAT/acrylic or methacrylic acid; DADMAC/acrylic or methacrylic acid copolymer

* a MES/acrylic or methacrylic acid/DMAEMA copolymer

* a MAPTAC/acrylic acid/acrylamide; MAPTAC/maleic anhydride/acrylamide; MAPTAC/vinylsulfonic acid/acrylamide copolymer

* a DADMAC/acrylic acid/acrylamide; DADMAC/maleic anhydride/acrylamide; DADMAC/vinylsulfonic acid/acrylamide copolymer

* a DIQUAT/acrylic acid/acrylamide; DIQUAT/maleic anhydride/acrylamide; DIQUAT/vinylsulfonic acid/acrylamide copolymer,

said copolymer having a ratio of the total number of anionic charges to the total number of cationic charges of from 95/5 to 5/95, very particularly from 90/10 to 10/90.

16) The use as claimed in any one of claims 13) to 15), characterized in that said dispersion comprises from 0.005 to 10%, preferably from 0.01 to 5%, very particularly from 0.01 to 2% by weight of said film-forming polymer capable of interacting with the surface of the titanium dioxide particles by electrostatic bonding.

17) The use as claimed in any one of claims 13) to 16), characterized in that said dispersion comprises water and has a pH of from 4 to 9.

18) A film-forming dispersion comprising

- from 0.01 to 15% of its weight, preferably from 0.1 to 10% of its weight of titanium dioxide in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g,

- and from 0.005 to 15% of its weight, preferably of the order of from 0.01 to 10% of its weight, of at least one film-forming polyalkoxylated organosiloxane or organic polymer,

the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is less than 120°C, preferably less than or equal to 100°C, and having, when it comprises water, a pH different by at least 1 unit, preferably at least 2 units, from the value of the isoelectric point of titanium dioxide in said dispersion.

19) The dispersion as claimed in claim 18), characterized in that the titanium dioxide is in the form of elementary particles whose size is of the order of from 20 to 60 nm and whose specific surface area is of the order of from 200 to 300 m^2/g.

20) The dispersion as claimed in claim 18) or 19), characterized in that the elementary particles of titanium dioxide are anatase.

21) The dispersion as claimed in any one of claims 18) to 20), characterized in that the alcohols

which may constitute or be present in the continuous phase are aliphatic monoalcohols whose boiling point is less than 100°C.

22) The dispersion as claimed in any one of claims 18) to 21), characterized in that the continuous phase comprises water.

23) The dispersion as claimed in claim 22) characterized in that the continuous phase comprises from 50 to 100%, preferably from 70 to 99.9% of water.

24) The dispersion as claimed in claim 22) or 23) characterized in that the dispersion has a pH of from 0 to 14, preferably from 2 to 14.

25) The dispersion as claimed in any one of claims 18) to 24), characterized in that said film-forming polymers are

- optionally sulfonated terephthalic oligoesters or copolyesters
- polyoxyalkylenated polymers which carry anionic functions
- cationic or amphoteric polymers
- polyalkoxylated polydimethylsiloxanes
- film-forming polymers derived from ethylenically unsaturated monomers polymerizable by radical means.

26) The dispersion as claimed in claim 25) characterized in that said polymer is capable of interacting with the surface of the titanium dioxide particles by electrostatic bonding.

27) The dispersion as claimed in claim 26)

characterized in that said film-forming polymer is

- a sulfonated terephthalic oligoester or copolyester
- a polyoxyalkylenated polymer which carries anionic functions, such as copolymers of acrylic acid and/or methacrylic acid and polyethylene glycol acrylate and/or methacrylate whose polyoxyethylene unit has a mass of from 500 to 10 000
- a cationic polymer additionally exhibiting bacteriostatic properties, such as
  - quaternary ammonium ionenes
  - cationic polymers derived from epichlorohydrin and dimethylamine and those derived from epichlorohydrin and imidazole
- a cationic homopolymer or copolymer derived from at least one cationic monomer containing ethylenic unsaturation: a monomer such as
  * aminoacryloyl or -acryloyloxy monomers such as trimethylaminopropyl methacrylate chloride, trimethylaminoethylacrylamide or -methacrylamide chloride or bromide, trimethylaminobutylacrylamide or -methacrylamide methyl sulfate, trimethylaminopropyl-methacrylamide methyl sulfate (MES), (3-methacrylamidopropyl)trimethylammonium chloride (MAPTAC), (3-acrylamidopropyl)trimethylammonium chloride (APTAC), methacryloyloxyethyl trimethylammonium chloride or methyl sulfate, and acryloyloxyethyltrimethylammonium chloride
  * 1-ethyl-2-vinylpyridinium bromide, chloride or methyl

sulfate

* N,N-dialkyldiallylamine monomers such as N,N-dimethyldiallylammonium chloride (DADMAC)

* polyquaternary monomers such as dimethylaminopropylmethacrylamide chloride, N-(3-chloro-2-hydroxypropyl)trimethylammonium (DIQUAT)

optionally in a mixture with at least one nonionic monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or methacrylates, polyoxyalkylene glycol acrylates or methacrylates

- an amphoteric copolymer derived from at least one cationic monomer containing ethylenic unsaturation, a monomer like those mentioned above, and at least one anionic monomer containing ethylenic unsaturation, such as

* acrylic, methacrylic, fumaric, maleic, itaconic, N-methacroylalanine, N-acryloylhydroxyglycine acids or anhydrides or their water-soluble salts

* water-soluble sulfonated or phosphonated ethylenically unsaturated monomers, such as sulfopropyl acrylate or its water-soluble salts, water-soluble styrene sulfonates, vinylsulfonic acid and its water-soluble salts or vinylphosphonic acid and its water-soluble salts

optionally in a mixture with at least one nonionic

monomer such as acrylamide, N-isopropylacrylamide, N,N-dimethylacrylamide, dimethylaminoethylmethacrylate (DMAEMA), dimethylaminopropylmethacrylamide, vinyl alcohol, alkyl or hydroxyalkyl acrylates or methacrylates, polyoxyalkylene glycol acrylates or methacrylates.

28) The dispersion as claimed in claim 27) characterized in that said cationic or amphoteric polymer derived from at least one cationic monomer containing ethylenic unsaturation is

* a DIQUAT homopolymer
* a DADMAC homopolymer
* a MAPTAC/acrylic or methacrylic acid; DIQUAT/acrylic or methacrylic acid; DADMAC/acrylic or methacrylic acid copolymer
* a MES/acrylic or methacrylic acid/DMAEMA copolymer
* a MAPTAC/acrylic acid/acrylamide; MAPTAC/maleic anhydride/acrylamide; MAPTAC/vinylsulfonic acid/acrylamide copolymer
* a DADMAC/acrylic acid/acrylamide; DADMAC/maleic anhydride/acrylamide; DADMAC/vinylsulfonic acid/acrylamide copolymer
* a DIQUAT/acrylic acid/acrylamide; DIQUAT/maleic anhydride/acrylamide; DIQUAT/vinylsulfonic acid/acrylamide copolymer,

said copolymer having a ratio of the total number of anionic charges to the total number of cationic charges of from 95/5 to 5/95, very particularly from 90/10 to

10/90.

29) The dispersion as claimed in any one of claims 26) to 28), characterized in that said dispersion comprises from 0.005 to 10%, preferably from 0.01 to 5%, very particularly from 0.01 to 2% by weight of said film-forming polymer capable of interacting with the surface of the titanium dioxide particles by electrostatic bonding.

30) The dispersion as claimed in any one of claims 26) to 29), characterized in that said dispersion comprises water and has a pH of from 4 to 9.

31) A process for cleaning and/or disinfecting surfaces exposed to light by depositing and then drying on said surfaces a film-forming titanium dioxide dispersion, said titanium dioxide being in the form of elementary particles whose size is less than 100 nm, preferably less than 70 nm, and whose specific surface area is greater than 150 m^2/g, preferably greater than 200 m^2/g, the continuous phase of said dispersion comprising water and/or at least one alcohol whose boiling point is lower than 120°C, preferably lower than or equal to 100°C, said dispersion having, when it comprises water, a pH different by at least 1 unit, preferably by at least 2 units, from the value of the isoelectric point of the titanium dioxide in said dispersion.

32) The process as claimed in claim 31), characterized in that the amount of titanium dioxide

deposited on the hard surfaces is of the order of from 0.01 to 10 g of titanium dioxide per m^2 of the surface to be treated, preferably of the order of from 0.05 to 5 g of titanium dioxide per m^2 of the surface to be treated.

33) The process for cleaning and/or disinfecting as claimed in claim 31) or 32), by deposition of the film-forming dispersion used as claimed in any one of claims 1) to 17) or claimed in any one of claims 18) to 30).

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (include Reference to PCT International Applications) PCT/FR00/00371	ATTORNEY'S DOCKET NO RN99013

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

USE OF FILM-FORMING TITANIUM DIOXIDE DISPERSIONS FOR CLEANING AND DISINFECTING SURFACES, FILM-FORMING TITANIUM DIOXIDE DISPERSIONS

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____

and was amended

on _____ (if applicable)

☒ was filed as PCT international application

Number **PCT/ FR00/00371**

on **February 15, 2000**

and amended under PCT ARTICLE 19

on _____(if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY PCT indicate PCT	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC 119
FRANCE	**99/01938**	**17 February 1999**	☒ **YES** ☐ **NO**
			☐ **YES** ☐ **NO**
			☐ **YES** ☐ **NO**
			☐ **YES** ☐ **NO**
			☐ **YES** ☐ **NO**

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONTINUED) include Reference to PCT International Applications) PCT/FR00/00371	ATTORNEY'S DOCKET NO RN99013

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations. §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120

U.S. APPLICATIONS		STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.

PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) **JOHN A. SHEDDEN - Reg. No. 25,644,**
Kevin McVEIGH – Reg. No. 33017
JOHN D. WOOD - Reg. No. 31,146

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203	FULL NAME OF INVENTOR	FAMILY NAME **GEFFROY**	FIRST GIVEN **Cédric**	SECOND GIVEN NAME
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201	SIGNATURE OF INVENTOR 202	SIGNATURE OF INVENTOR 203
DATE August 20th, 2001	DATE 7th of August 2001	DATE 6th of August 2001

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONTINUED) include Reference to PCT International Applications) PCT/FR00/00371	ATTORNEY'S DOCKET NO RN99013

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations. §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120

U.S. APPLICATIONS		STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED

PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) **JOHN A. SHEDDEN - Reg. No. 25,644,**
Kevin McVEIGH – Reg. No. 33017
JOHN D. WOOD - Reg. No. 31,146

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	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true: and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 204	SIGNATURE OF INVENTOR 205	SIGNATURE OF INVENTOR 206
DATE 22 of August 2001	DATE 02 August 2001	DATE